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(54) Title of the Invention: HIGH-GRADE SECONDARY ALCOHOL ALCOXYLATE AND ITS DERIVATIVE COMPONENTS, AS WELL AS THE MANUFACTURING METHODS AND THE DETERGENTS AND EMULSIFIERS THAT USE THEM.

(57) Abstract (With Corrections)

Problem

To provide a high-grade secondary alcohol alkoxylate having superior detergent/emulsification capacity, good defoaming and permeation characteristics that has a low flow point and is easy to

work with. To provide a method for manufacturing said substance, its derivative compositions and to provide detergents and emulsifiers that use them.

## Means of Solving Problem: General Formula 1

/formula/

(1)

Where  $R^1$  and  $R^2$  represent alkyl groups, the carbon numbers of  $R^1$  and  $R^2$  total 7 to 29, and  $R^2$  is greater than or equal to the carbon number of  $R^1$ . "A" is a low-grade alkylene group. "n" averages between 1 and 50 and when "n" is equal to 2 or more, there is to be one or more types of AO. When there are two or more types, there is to be an average number of "n" units overall. Of the high-grade, secondary alcohol alkoxylates, olefin compounds having carbon atom numbers of C8 to 30 and alpha-olefin/inner olefin mol ratios of 80/20 to 0/100 and (poly) alkylene glycol having carbon atom numbers of C2 to 8, will be added to the high-grade, secondary alcohol alkoxylate compositions and their alkylene oxide addition compositions consisting of 30 to 90 mol% (X), where  $R^1$  is a methyl group, and 10 to 70 mol% (Y) or where  $R^1$  is at least C2.

## Scope of Patent Claims

**Claim 1**      **General Formula**      (1)

### Chemical Formula 1

/formula/

(1)

Where  $R^1$  and  $R^2$  represent alkyl groups and the total number of carbon atoms in  $R^1$ , the number of carbon atoms in  $R^2$  is between 7 and 29 and the number of carbon atoms in  $R^2$  is greater than or equal to the number of carbon atoms in  $R^1$ . "A" represents a low-grade alkylene group and "n" averages between 1 and 50. However, when "n" is equal to 2 or more, 1, 2 or more types of oxyalkylene groups, expressed by AO, may be used and, when the number of types of said oxyalkylene groups is 2 or more, each type of oxyalkylene group is to have an average of "n" units overall. Of the high-grade, secondary alcohol alkoxylates expressed this way, olefin compounds having carbon atom numbers of 8 to 30 and which have alpha-olefin/inner olefin mol ratios of 80/20 to 0/100 and (poly) alkylene glycol having carbon atom numbers of 2 to 8, will be added to those high-grade, secondary alcohol alkoxylate compositions made up of 30 to 90 mol % high-grade, secondary alcohol alkoxylate (X), for which  $R^1$  is a methyl group and 10 to 70 mol % high-grade, secondary alcohol alkoxylate (Y) where  $R^1$  is an alkyl group with a carbon atom number of 2 or more, producing high-grade, secondary alcohol alkoxylate compositions.

### Claim 2

The composition described in Claim 1 where the aforementioned (poly) alkylene glycol is ethylene glycol.

**Claim 3**

The compositions described in Claim 1 or Claim 2, which are sulfated and neutralized, producing a high-grade secondary alcohol alkoxylate sulfuric acid ester.

**Claim 4**

Alkylene oxides with carbon atom numbers of 2 to 8 are added to the compositions described in Claim 1 or Claim 2, producing a high-grade, secondary alcohol alkoxylate composition to which alkylene oxides have been added.

**Claim 5**

The composition described in Claim 4, where the aforementioned alkylene oxide is an ethylene oxide.

**Claim 6**

The compositions described in Claim 4 or Claim 5, which are sulfated and neutralized, producing a sulfated ester composition of high-grade, secondary alcohol alkoxylate to which alkylene oxide has been added.

**Claim 7**

A detergent containing the compositions described in Claims 1 through 6.

**Claim 8**

An emulsifier containing the compositions described in Claims 1 through 6.

**Claim 9**

General Formula (1)

Chemical Formula 2

/formula/

(1)

Where  $R^1$  and  $R^2$  represent alkyl groups, the total of the carbon atom numbers of  $R^1$  and of  $R^2$  is 7 to 29 and where the carbon atom number of  $R^2$  is greater than or equal to that of  $R^1$ . "A" represents a low-grade alkylene group and "n" averages 1 to 50. However, when "n" is greater than 2, there may be 1, 2 or more types of oxyalkylene groups expressed as AO. If there are two or more types of these oxyalkylene groups, then "n" indicates that each oxyalkylene group in question has an average of "n" units overall. Of the high-grade, secondary alcohol alkoxylates expressed in this way, there will be high-grade, secondary alcohol alkoxylate compositions made up of 30 to 90 mol % high-grade, secondary alcohol alkoxylate (X) (where  $R^1$  is a methyl group) and 10 to 70 mol % high-grade, secondary alcohol alkoxylate (Y) (where  $R^1$  is an alkyl group having a carbon atom number of 2 or more). Methods of manufacturing high-grade, secondary alcohol alkoxylate compositions in which olefin compounds having an alpha-olefin/inner olefin mol ratio of 80/20 to 0/100 and carbon atom number of 8 to 30 are added with (poly) alkylene glycol having a carbon atom number between 2 and 8 to the manufacturing method described above.

**Claim 10**

A method for manufacturing sulfated ester salt compositions of high-grade, secondary alcohol alkoxylates characterized by sulfating and neutralizing the high-grade, secondary alcohol alkoxylate composition obtained using the manufacturing method described in Claim 9.

**Claim 11**

A method for manufacturing compositions of high-grade, secondary alcohol alkoxylates, to which alkylene oxides have been added, characterized by addition of alkylene oxides having carbon atom numbers of 2 through 8 to the high-grade, secondary alcohol alkoxylate composition obtained using the manufacturing method described in Claim 9.

**Claim 12**

A method for manufacturing sulfated ester salt compositions to which high-grade, secondary alcohol alkoxylate alkylene oxides are added, characterized by sulfating and neutralizing high-grade, secondary alcohol alkoxylate compositions, obtained using the manufacturing methods described in Claim 11, to which alkylene oxides have been added.

**Detailed Description of the Invention**

0001

**Technical Fields of the Invention**

This invention pertains to high-grade, secondary alcohol alkoxylates, their derivative compositions, the methods of manufacturing them, and detergents and emulsifiers that use them.

0002

**Prior Art**

Nonionic surfactants contain alkyl phenol ethoxylates, high-grade, primary alcohol ethoxylates, fatty acid ethoxylates and other substances. Of these, the alkyl phenol ethoxylates and, particularly, the nonyl phenol ethoxylates, have a detrimental effect on the environment due to poor biodegradability and they tend to be regulated. Also, high-grade, primary alcohol ethoxylate has a high flow point so that not only does it harden at room temperature, but it also lacks sufficient permeation capacity and other surfactant qualities. Furthermore, it has insufficient detergent and emulsifying strength. The use of other nonionic surfactants such as fatty acid ethoxylate is restricted. For example, the inability to use them in an alkali state due to their hydrolytic characteristics. They also lack sufficient performance characteristics.

0003

In contrast, high-grade, secondary alcohol alkoxylate, which is a nonionic surfactant, is useful for its low flow point, handling ease, excellent capacity for permeation, good foam reduction and superior detergent and emulsifying capacity. Be that as it may, however, traditional manufacturing methods use liquid phase conversion of a normal chain paraffin made from a mix of 1, 2 or more hydrocarbons having a carbon atom number of 8 to 20, producing a random secondary alcohol. A Lewis acid catalyst is then used on it while ethylene oxide is added, producing a low-ethylene oxide additive. Unreacted alcohol is then recovered from this reaction mixture and then ethylene oxide is added using a basic (as opposed to acidic) catalyst.

With this sort of method, not only must you add ethylene oxide once to produce the ethoxylate, the catalysts must be removed, distilled and then ethylene oxide must be added. The process is extremely complex.

0004

There are various types of negative ion surfactants, including alkyl aryl sulfonate, high-grade, primary alcohol ester sulfate and high-grade, primary alkyl ether ester sulfate. Of these, alkyl aryl sulfonate and, in particular, normal-chain alkyl benzene sulfonate have poor biodegradability, so they have a deleterious effect on the environment. Because of this, there is a tendency to regulate them. Alkyl aryl sulfonate, high-grade, primary alcohol ester sulfonate and the like are easily affected by hardness and have poor solubility in water. Not only does high-grade, primary alkyl ether ester sulfate have high viscosity and gel easily, it also lacks sufficient surface tension and permeation capacity so it doesn't perform well enough as a surfactant. It also lacks sufficient detergent and emulsifying strength. There are no other negative ion surfactants with performance characteristics that are good enough.

0005

In contrast, high-grade, secondary alkyl ether ester sulfate, which is a negative ion surfactant, has a low viscosity and does not gel easily so it is easier to work with and it has excellent surface tension and permeation capacity. It is also useful for its good defoaming characteristics, detergent strength and emulsifying capacity. Be that as it may, however, in traditional production methods, normal chain paraffins are obtained from a mix of 1, 2 or more hydrocarbons having a carbon atom number from 8 to 20 using liquid phase oxidation. A Lewis acid catalyst is used on a random secondary alcohol, to which ethylene oxide is added, producing a low ethylene oxide additive. The unreacted alcohol is then recovered from this reaction mixture and then ethylene oxide is added using a basic (as opposed to acidic) catalyst. Next, chlorosulfonate or anhydrous sulfuric acid are used in sulfation. While high-grade, secondary alkyl ether sulfur ester salt can be produced using this method, it requires not only that ethylene oxide be added once, but also requires removing the catalyst, distillation and the further addition of ethylene oxide and then sulfation. The process remains extremely complex.

0006

#### Problems that the Invention Attempts to Resolve

In this way, the objective of this invention is to provide a new high-grade, secondary alcohol alkoxylate or a derivative composition, production methods and detergents and emulsifiers using them.

0007

Another purpose of this invention is to provide a high-grade, secondary alcohol alkoxylate with superior detergent strength and emulsifying capacity, defoaming characteristics and excellent permeation characteristics that is easy to work with and has a low flow point. It will also provide a method for producing these as well as detergents and emulsifiers using these.

0008

Means for Resolving the Problems

The above objectives can be achieved by the high-grade, secondary alcohol alkoxylate of this invention and its derivative compositions, their manufacturing methods and the detergents and emulsifiers using them.

0009

That is, this invention uses the general formula (1)

0010

Chemical Formula 3

/formula/

(1)

0011

Where  $R^1$  and  $R^2$  represent alkyl groups, the carbon atom numbers of  $R^1$  and  $R^2$  are between 7 and 29 and the carbon atom number of  $R^2$  is greater than or equal to the carbon atom number of  $R^1$ . "A" represents a low-grade alkylene group and "n" is between 1 and 50 on average. However, when "n" is 2 or more, there may be 1, 2 or more types of oxyalkylene groups (represented by AO) and when there are 2 or more types of said oxyalkylene groups, "n" indicates the average number of each type of oxyalkylene group overall.

This is a high-grade, secondary alcohol alkoxylate composition produced as below and it has the following characteristics.

Of the high-grade, secondary alcohol alkoxylates expressed this way, when  $R^1$  is a 30 to 90 mol %, high-grade, secondary alcohol alkoxylate (X), which is a methyl group, and  $R^1$  is a high-grade, secondary alcohol alkoxylate composition made using 10 to 70 mol % high-grade, secondary alcohol alkoxylate (Y), which is an alkyl group with a carbon atom number of 2 or more, then the composition will be produced by the addition of (poly) alkylene glycol having a carbon atom number of 2 to 8 and an olefin compound having a mol ratio of 80/20 to 0/100 (alpha-olefin/inner olefin) and a carbon atom number of 8 to 30.

0012

In this invention, the aforementioned (poly) alkylene glycol is the aforementioned composition, which is ethylene glycol.

0013

This invention is also a high-grade, secondary alcohol alkoxylate sulfuric acid ester salt produced by sulfating and neutralizing the composition described above.

0014

Again, this invention is a compound of high-grade, secondary alcohol alkoxylates with alkylene oxides added that is produced by adding alkylene oxides having a carbon atom number of 2 to 8 to the composition described above.

0015

This invention is also the aforementioned composition where the alkylene oxide described above is ethylene oxide.

0016

This invention is also a sulfuric acid ester salt composition of high-grade, secondary alcohol alkoxylate to which alkylene oxide has been added by sulfating and neutralizing the composition described above.

0017

This invention is a detergent that contains the composition described above.

0018

This invention is an emulsifier that contains the composition described above.

0019

This invention also uses the general formula (1)

0020

Chemical Formula 4

/formula/

(1)

0021

Where  $R^1$  and  $R^2$  represent alkyl groups, the carbon atom number of  $R^1$  and  $R^2$  are between 7 and 29 and the carbon atom number of  $R^2$  is greater than or equal to the carbon atom number of  $R^1$ . "A" represents a low-grade alkylene group and "n" is between 1 and 50 on average. However, when "n" is 2 or more, there may be 1, 2 or more types of oxyalkylene groups (represented by AO) and when there are 2 or more types of said oxyalkylene groups, "n" indicates the average number of each type of oxyalkylene group overall.

This is a high-grade, secondary alcohol alkoxylate composition produced as below and it has the following characteristics.

Of the high-grade, secondary alcohol alkoxylates expressed this way, when  $R^1$  is a 30 to 90 mol %, high-grade, secondary alcohol alkoxylate (X), which is a methyl group, and  $R^1$  is a high-grade, secondary alcohol alkoxylate composition made using 10 to 70 mol % high-grade, secondary alcohol alkoxylate (Y), which is an alkyl group with a carbon atom number of 2 or more, then the composition will be produced by the addition of (poly) alkylene glycol having a carbon atom number of 2 to 8 and an olefin compound having a mol ratio of 80/20 to 0/100 (alpha-olefin/inner olefin) and a carbon atom number of 8 to 30.

0022

This invention is also a method for producing high-grade, secondary alcohol alkoxylate sulfuric acid ester salt compositions that are prepared using the methods described above in which a high-grade, secondary alcohol alkoxylate composition is sulfated and neutralized.

0023

Moreover, this invention is a method of producing high-grade, secondary alcohol alkoxylates to which alkylene oxides have been added by using high-grade, secondary alcohol alkoxylates produced using the methods described above and adding alkylene oxides having carbon atom numbers from 2 to 8.

0024

This invention is also a method of manufacturing sulfuric acid ester salt compositions to which high-grade, secondary alcohol alkoxylates have been added by sulfating and neutralizing alkylene oxide added compositions of high-grade, secondary alcohol alkoxylate, produced using the methods described above.

0025

#### Embodiments of the Invention

This invention also uses the general formula (1)

0026

#### Chemical Formula 5

/formula/

(1)

0027

Where  $R^1$  and  $R^2$  represent alkyl groups, the carbon atom number of  $R^1$  and  $R^2$  is between 7 and 29 and the carbon atom number of  $R^2$  is greater than or equal to the carbon atom number of  $R^1$ . "A" represents a low-grade alkylene group and "n" is between 1 and 50 on average. However, when "n" is 2 or more, there may be 1, 2 or more types of oxyalkylene groups (represented by AO) and when there are 2 or more types of said oxyalkylene groups, "n" indicates the average number of each type of oxyalkylene group overall.

This is a high-grade, secondary alcohol alkoxylate composition, its compounds to which alkylene oxides have been added, their sulfuric acid ester salt compositions, their manufacturing methods as well as the detergents and emulsifiers produced using them.

Among the high-grade, secondary alcohol alkoxylates expressed this way are those where  $R^1$  is a 30 to 90 mol %, high-grade, secondary alcohol alkoxylate (X), which is a methyl group and those where  $R^1$  is a high-grade, secondary alcohol alkoxylate (Y), which is an alkyl group with a carbon atom number of 2 or more. They also include their alkylene oxide addition compositions, their ester sulfate salt compositions, their manufacturing methods and the detergents and emulsifiers that use them.

0028

In the above general formula (1), the low-grade alkylene group expressed by "A" is an alkylene group with a carbon atom number of 2 to 8 or preferably with a carbon atom number of 2 to 4. In the same way, the oxyalkylene group expressed using "AO" could be, for example, an ethoxy group, a propoxy group, a butoxy group, an isopropoxy group, a pentyl oxy group, a hexyl oxy group, a heptyl oxy group, an octal oxy group or similar group. Preferably, it will be an ethoxy group, propoxy group or butoxy group. According to the definition of "AO" in the

general formula (1) above, these oxyalkylene groups may be made up of just one type, but they may also be made up of two or more types. If the oxyalkylene groups are to be composed of two or more types, the two or more types of oxyalkylene groups may be arranged in random fashion and they may be arranged in their respective blocks. For example, a portion of the ethoxy group's long chain may be composed of propoxy groups.

0029

In the above general equation (1), the alkyl groups represented by  $R^1$  and  $R^2$  should preferably be normal chain alkyl groups. The total of the carbon atom numbers of  $R^1$  and  $R^2$  should be between 7 and 29 and a range of 9 to 19 would be preferred. In addition, the carbon atom number of  $R^1$  is to be higher than the carbon atom number of  $R^2$  (carbon atom number of  $R^1 \leq$  carbon atom number of  $R^2$ ).

0030

In the above general formula, "n" averages from 1 to 50 or preferably, from 1 to 20.

0031

For the high-grade, secondary alcohol alkoxylate composition of this invention,  $R^1$  is the 30 to 90 mol % (preferably 40 to 80 mol %) high-grade, secondary alcohol alkoxylate (X), which is a methyl group, and  $R^1$  is the 10 to 70 mol % (preferably 20 to 60 mol %) high-grade, secondary alcohol alkoxylate (Y), which is an alkyl group having a carbon atom number of 2 or more, in the high-grade, secondary alcohol alkoxylate expressed using the general formula (1). The high-grade, secondary alcohol alkoxylate composition that has a ratio of the high-grade, secondary alcohol alkoxylate (X) to the high-grade, secondary alcohol alkoxylate (Y) within the range described above will have either no gelification range or an extremely narrow one in an aqueous solution having a low fusion point. It will have excellent handling characteristics, good permeation characteristics, good defoaming and excellent detergent and emulsification capacities. If the ratio of the high-grade, secondary alcohol alkoxylate (X) exceeds 90 mol %, the high-grade, secondary alcohol alkoxylate composition that is produced will have a higher flow point and less detergent capacity. In contrast, if the ratio of the high-grade, secondary alcohol alkoxylate (X) is less than 30 mol %, the performance as a surfactant will be about the same, but it would increase the manufacturing methods used with this invention, eliminating any economic advantage.

0032

The high-grade, secondary alcohol alkoxylate composition of this invention described above was produced using an addition reaction of a long-chain olefin with a carbon atom number of 8 to 30, an olefin mixture with an alpha-olefin/inner olefin mol ratio of 80/20 to 0/100 and a (poly) alkylene glycol with a carbon atom number from 2 to 8, in the presence of an acid catalyst. The resulting product was distilled, extracted and separated using other methods.

0033

In this invention, the long-chain olefin used in the above olefin mixture was an acyclic hydrocarbon that had an ethylene-based unsaturated bond and a carbon atom number from 8 to 30 (preferably from 10 to 20). Specific examples of such olefins include octene, decene, dodecene, tetradecene, hexadecene, octadecene, eicosene, docosene, tetracosene, hexacosene,

octacosene, and triacosene, for example 1-decene, 2-decene, 1-dodecene, 2-dodecene, 3-dodecene, 4-dodecene, 5-dodecene, 1-tetradecene, 2-tetradecene and 1-hexadecene. Of these, decene, dodecene, tetradecene, hexadecene, octadecene and eicosene are preferred for use.

0034

For the long-chain olefins used in the addition reactions described above, it is best to use mixed olefins where the mol ratio of the alpha-olefin, which has an unsaturated bond at the alpha position, and the inner olefin, which has a double bond at an inner position (a position other than the alpha position), is in a range of 80/20 to 0/100 (preferably 50/50 to 5/95). By using mixed olefins with a mol ratio within the above range, the high-grade, secondary alcohol alkoxylate composition of this invention can be produced with an economic advantage. If the above mol ratio does not meet the minimum limits above, the olefin reactivity will degrade, requiring a larger reactor, which is undesirable. Again, if the maximum limits of the above mol ratios are exceeded, the high-grade, secondary alcohol alkoxylate composition produced by the addition reaction will be affected as follows. The R<sup>1</sup> in the general formula (1) above will exceed the upper limit of the content of the high-grade, secondary alcohol alkoxylate (X) (which is a methyl group), of 90-mol %. This will reduce performance characteristics such as flow, permeation and detergent capacity, which is undesirable. More specifically, for example, it would be possible to use an olefin mixture where both elements were adjusted to within the above range by heat treating the alpha-olefin in a temperature range of around 80 to 200° C in the presence of an acid or base catalyst, so that some of the alpha-olefin or an olefin mixture of commercially available inner olefin and alpha olefin that had been mixed to the above range were isomerized. Normally, unreacted olefins will remain after the addition reaction, so the ratio of alpha-olefins to inner olefins could be adjusted to the above range when recovering, circulating and reusing these unreacted olefins.

0035

It is desirable to use a (poly) alkylene glycol that has a carbon atom number from 2 to 8 in the above addition reactions. Specific examples of this sort of (poly) alkylene glycol include monoethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, monopropylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, 1, 3-propane diole, 1, 2-butane diole, 2, 3-butane diole, 1, 4-butane diole, 1, 6-hexane diole, paraxylene glycol and 1, 4-cyclohexane methane diole. These may be used alone or with 2 or more other types in a mixed state.

0036

Here, the mol ratio of the (poly) alkylene glycol described above in relation to the olefin mixture described above is not particularly restricted, but it is desirable to keep it from 0.05 to 20 and preferable to keep it from 0.1 to 10. If this mol ratio is less than 0.05, the high-grade, secondary alcohol alkoxylate yield will fall. At the same time, if it exceeds 20, the volume of the reactor will become greater, making it uneconomical, which is undesirable. Normally, for the addition reaction conditions for the olefin mixture and the (poly) alkylene glycol described above, the reaction temperature ranges from 50 to 250° C (preferably 100 to 200° C), the reaction pressure may be either a vacuum, normal pressure or pressurized, but a range from normal pressure to 20 kg/cm<sup>2</sup> is desirable. If the above reaction temperature is less than 50° C, the reaction speed will be too slow. On the other hand, if it exceeds 250° C, the olefins will

polymerize, the (poly) alkylene glycol will decompose or degenerate. This is undesirable because the selectivity will be reduced.

0037

Specific examples of acid catalysts used in the reaction of this olefin mixture and the (poly) alkylene glycol include highly acidic ion exchange resins, BEA zeolite and other crystalline alumino silicates, dodecyl sulfonate and others, but based on its reactivity, a crystalline alumino silicate would be preferred. Of those, the BEA zeolite is desirable.

0038

In relation to the aforementioned olefin mixture, the amount of such acid catalysts should be 1 to 50 wt % (preferably 2 to 30 wt %). Sufficient catalytic capacity is not possible when the amount of said catalyst is less than 1 wt %. Amounts in excess of 50 wt % are undesirable because the full effect of the addition of higher amounts cannot be realized, which is uneconomical.

0039

Next, the high-grade, alcohol alkoxylate addition composition made with the secondary alcohol alkoxylate of this invention can be produced through an addition reaction in the presence of an alkali catalyst, in which alkylene oxide having a carbon atom number of 2 to 8 is added to the above high-grade, secondary alcohol alkoxylate combination.

0040

The alkylene oxide used in the alkylene oxide addition composition of the high-grade, secondary alcohol alkoxylate of this invention should have a carbon atom number of 2 to 8 (preferably 2 to 4). Specific examples of this sort of alkylene oxide include ethylene oxides, propylene oxides, butylene oxides and styrene oxides.

0041

The mol count of the alkylene oxide is not particularly limited in the addition reaction above, but a range of 1 to 30 is desirable, while a range of 4 to 20 is more desirable. Conditions for adding this alkylene oxide include a reaction temperature that is normally in a range of 50 to 250° C (preferably 100 to 200 ° C), a normal or pressurized reaction pressure may be used, but a range from normal pressure to 20 kg/cm<sup>2</sup> is desirable. If the reaction temperature described above is less than 50° C, the reaction speed will decline. On the other hand, temperatures in excess of 250° C are undesirable because breakdowns and the number of byproducts will increase.

0042

Examples of the alkali catalyst mentioned above include element oxides belonging to the alkali earth metals or alkali metals. For instance, sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, calcium hydroxide and barium hydroxide. Based on availability and reactivity, sodium hydroxide and potassium hydroxide would be desirable. These may be used in a powder or granular state and added in an aqueous solution or dehydrated. The amount of this alkali catalyst to be used should be 0.01 to 2.0 wt % (in relation to the feedstock alkoxylate), while a range 0.02 to 0.5 wt % would be preferred.

0043

The high-grade, secondary alcohol alkoxylate compositions and alkylene oxide addition sulfuric acid ester salt compositions of this invention may be sulfated using chlorosulfonic acid. By neutralizing the resulting reaction solution with a basic (nonacid) substance, or, by sulfating the high-grade, secondary alcohol alkoxylate compositions or the alkylene oxide addition compositions in the presence of a solvent, the resulting reaction solution can be neutralized using a basic (nonacid) substance and finished by removing that solvent.

0044

The chlorosulfonic acid used in sulfonation may be added to the high-grade, secondary alcohol alkoxylate composition or the alkylene oxide addition composition using known methods. For example, it may be dripped directly or with air or an inert gas. A sulfonation device equipped with external circulation line mixture such as the one described in JSP H01 – 036823 could be used for mixing. This would allow batch style sulfonation. The chlorosulfonic acid should be dripped for 1 to 2 hours and the reaction temperature should range from –20 to 30° C (preferably 0 to 20° C).

0045

Also, when using anhydrous sulfuric acid for sulfation, known methods, such as those described in JSP S51-17538, are to be used with a parallel flow, thin-film reactor so that the high-grade, secondary alcohol alkoxylate compositions or alkylene oxide addition compositions flow out in a thin-film state. Continuous sulfation would be possible by using a parallel flow of anhydrous sulfuric acid gas diluted with an inert gas to effect gas-liquid contact. The speed of the inert gas should be about 20 to 70 m per second and the concentration of anhydrous sulfuric acid should be 1 to 10 wt %. For the mol ratio of the anhydrous sulfuric acid to the high-grade, secondary alcohol alkoxylate, a range of 0.95 to 1.2 is desirable. A reaction temperature of –20 to 60° C (especially 0 to 30° C) is desirable.

0046

Using a solvent in the sulfation process makes it possible to produce even higher yields of high-quality high-grade, secondary alcohol alkoxylates or alkylene oxide addition sulfuric acid ester salt compositions with this invention. Possible solvents include chloroform, carbon tetrachloride, ethyl chloride, ethylene chloride, 1, 1, 1-trichloroethane, 1, 1, 1, 2-tetrachloroethane or other chlorine-based solvents; n-pentane, n-hexane, n-heptane, cyclohexane or other hydrocarbon solvents; diethyl ether, isopropyl ether or other ether solvents. A solvent concentration in the reaction solution of 10 to 90 wt % is desirable. If the solvent concentration is less than 10 wt %, using a solvent will not produce an effect and, if it exceeds 90 wt %, the reaction efficiency will decline, leading to lower yields, which would be undesirable.

0047

Basic substances that are suitable to the above neutralization process include alkali metal hydroxides or, preferably, sodium hydroxide, potassium hydroxide or lithium hydroxide. More desirable would be magnesium oxide, magnesium hydroxide, calcium oxide or calcium hydroxide, ammonia, alkanol amine or, more preferably, mono- di- or tri ethanol amine. For alkyl groups, primary, secondary and tertiary alkyl amines that contain 1 to 4 carbon atoms are desirable.

0048

Uses for the high-grade, secondary alcohol alkoxylates of this invention and their derivatives include, for example, in addition to nonionic surfactant, anionic surfactant and cationic surfactant manufacturing feedstocks. It is also desirable to use them as detergents and emulsifiers based on their low flow point, ease of handling, excellent permeation capacity, good defoaming and superior detergent and emulsification capacity.

0049

When using the high-grade, secondary alcohol alkoxylate and its derivative compositions as detergent agents, the above high-grade, secondary alcohol alkoxylate and its derivative compositions may be used individually or they may be used in conjunction with known detergent surfactants. Examples of these sorts of surfactants include alkyl benzene sulfonate, alkyl sulfuric acid ester salt, alpha-olefin sulfonate, alkyl sulfonate, aliphatic amide sulfonate, dialkyl sulfosuccinate, alkyl ether sulfuric acid ester salt or other negative ion surfactants, alkyl amine salt, class 4 ammonium salt or other positive ion surfactants, alkyl betaine or other amphotionic surfactants.

0050

It would be possible to use the high-grade, secondary alcohol alkoxylate or its alkylene oxide addition compositions in conjunction with known non-ionic surfactants such as high-grade primary alcohol ethoxylates as long as the range does not obstruct the basic detergent performance of the invention.

0051

The high-grade, secondary alcohol alkoxylate and the alkylene oxide addition sulfuric acid ester salt compositions of this invention may be used in conjunction with known negative ion surfactants such as alkyl aryl sulfonate, high-grade primary alcohol sulfuric acid ester salts or high-grade primary alkyl ether sulfuric acid ester salts as long as their use remains in a range that does not obstruct the basic detergent performance of the invention.

0052

Moreover, all sorts of additives that are used in normal detergents may be used with the detergents of this invention. Such additives include, for example, alkali agents, builders, perfumes, fluorescent whiteners, dyes, foaming agents, foaming stabilizers, polishing agents, anti-bacterial agents, bleaching agents, enzymes, preservatives, dyes and solvents.

0053

The detergent of this invention can be used effectively in detergents for clothing, textile goods, utensils, containers, miscellaneous equipment, foods, building maintenance products, homes, furniture, aircraft, and metal products as well as in shampoos and body shampoos.

0054

Also, when using the high-grade, secondary alcohol alkoxylate and its derivative compositions as emulsifiers, the high-grade, secondary alcohol alkoxylate compound compositions may be used individually or they may contain known emulsifiers. For example,

they could be used with the negative ion surfactants, positive ion surfactants, nonionic surfactants or amphionic surfactants generally used as emulsifiers.

0055

There are no particular restrictions when using oil-based substances in the emulsifiers of this invention and mineral oils, animal or vegetable oils or synthetic oils may be used. These may be used individually or 2 or more may be mixed together. Examples of mineral oils include, for example, spindle oil, machine oil and liquid paraffin. Typical animal and vegetable oils include beef fat, pork fat, fish oil, whale oil, rapeseed oil, sesame oil, coconut oil, soybean oil, palm oil, camellia oil and castor oil.

0056

The emulsifiers of this invention can be used in agricultural chemicals, metal-processing oils, paints and emulsifying emulsion polymers.

0057

Embodiments

Embodiments are used in the detailed description of the invention that follows below. This invention is not restricted to these embodiments. Moreover, for the following embodiments, substances where "n" is 1 in the general formula (1) described above shall be referred to as high-grade, secondary alcohol alkoxylates while those where "n" is 2 or more shall be called high-grade, secondary alcohol alkoxylate alkylene oxide additions.

0058 (Method of Synthesis)

Embodiment 1

BEA zeolite manufactured by PQ, Inc. (product name: VALFOR CP811 BL-25) containing 5 wt % secondary dodecanol ethoxylate composition 1-dodecene was reacted for 10 hours at 150° C in a liquid state. 810 g (4.82 mol) of the resulting dodecene isomer mixture (composed of 25 mol % 1-dodecene and 75 mol % inner dodecene) 900 g (14.52 mol) of monoethylene glycol and 100 g of BEA zeolite (manufactured by PQ, Inc., product name: VALFOR CP 811 BL-25) as a catalyst were placed in a glass reactor equipped with stirring paddles and cyclical flow cooling. After replacing the gaseous state portion with nitrogen, the mixture was held at normal pressure in a nitrogen atmosphere. Next, the temperature was increased to 150° C while stirring at a speed of 600 rpm. After reacting for 3 hours at that temperature, the reaction solution was cooled to room temperature, the upper dodecene phase layer separated off and the mix was distilled. After distilling away the unreacted dodecene, the mix was held in a boiling point range of 129 to 131° C in a vacuum of 2mmHg, yielding 155 g of a high-grade, secondary dodecanol ethoxylate composition.

0059

The <sup>1</sup>H-NMR analysis (FIG. 1) revealed the following about the alkyl chain carbon addition position of the ethoxylation site of the high-grade, secondary dodecanol ethoxylate compositions produced. The results of the calculations using the proton ratio of the alkyl terminal methyl group showed that the percentage of the secondary alcohol ethoxylate composition in which the second position was ethoxylated (The R<sup>1</sup> in the General Formula (1) is an ethoxylate, which is a methyl group.) (The high-grade, secondary alcohol alkoxylate

compound (X) described above and in the same way below) was 71 mol %. The flow point of this secondary alcohol ethoxylate composition we measured according to JIS K-2269 at -20° C.

0060

Method of Calculating the Position of the Ethoxylation or the Sulfuric Acid Ester Salt.

"a" is the integral value of the double line around 1.15 ppm. (If R<sup>1</sup> is a methyl group, the proton of the R<sup>1</sup> methyl group.)

"b" is the integral value of the triple line around 0.9 ppm. (The terminal methyl group of R<sup>1</sup> when R<sup>1</sup> is an alkyl group with a carbon atom number of 2 or more as well as all R<sup>2</sup> terminal methyl group protons.)

"c" is the ratio of the high-grade, secondary alcohol alkoxylate compound (X).

$$c = 2a / (a + b)$$

NMR Measuring Method

Equipment Type: Varian UNITY Plus 400 (400 MHz)

Solvent: CDCl<sub>3</sub> + 0.03% TMS : Sample = 99 : 1

Number of Iterations: 16

The conditions indicated after the <sup>1</sup>H-NMR measurements were as follows.

0061

Frequency: 399.958 MHz

Spectral Width: 7998.4 Hz

Acquisition Time: 4.001 sec

Relaxation Delay 3.000 sec

Pulse Width 10.0 usec

Ambient Temperature

No. Repetitions: 16

Double Precision Acquisition

Data Processing

FT Size 65536

Total Acquisition Time: 1 minute

Embodiment 2: Secondary Dodecanol Ethoxylate Ethylene Oxide Addition Composition

155 g (0.67 mol) of the high-grade, secondary dodecanol monoethoxylate produced in Embodiment 1 and 0.2 g of sodium hydroxide as a catalyst were placed in a stainless steel autoclave. After nitrogen substitution and heating to 150° C at 1.0 kg/cm<sup>2</sup> G, 217 g (4.93 mol) of ethylene oxide was run into the autoclave. After the ethylene oxide, the substance was maintained at 150° C for another hour, cooled to room temperature and, after purging the internal pressure, the secondary dodecanol ethoxylate ethylene oxide addition composition in the General Formula (1) was produced with "n" averaging 8.4.

0062

The alkyl chain carbon addition position of the ethoxylate site of the secondary dodecanol ethoxylate ethylene oxide addition composition was calculated using <sup>1</sup>H-NMR analysis (FIG. 2) and the proton ratio of the alkyl terminal methyl group. The percentage of the

secondary alcohol ethoxylate ethylene oxide addition with the ethoxylated second position was 72 mol %. The NMR measurement methods and the calculation of the ethoxylation position were carried out just as for Embodiment 1.

0063

**Embodiment 3: Secondary Tetradecanol Ethoxylate Composition**

1-tetradecene and 5 wt % of BEA zeolite (manufactured by PQ, Inc., Product Name: VALFOR CP 811 BL-25) were reacted in a liquid phase at 150° C for 13 hours. 810 g (4.13 mol) of the resulting tetradecene isomer mixture (composed of 20 mol % 1-tetradecene and 80 mol % inner tetradecene), 900 g (14.52 mol) of monoethylene glycol and 100 g of BEA zeolite (manufactured by PQ, Inc., Product Name: VALFOR CP 811 BL-25) as a catalyst were placed in a 3000 ml glass reactor, which was equipped with stirring paddles and a circulating cooling system. After replacing the gas with nitrogen, it was held in a nitrogen atmosphere at normal pressure. It was then heated to 150° C while being stirred at a speed of 600 rpm and then reacted for 3 hours at that temperature. The reaction solution was then cooled to room temperature and the upper tetradecene phase layer was separated off and distilled.

0064

After removing the unreacted tetradecene, 102 g of a second tetradecanol ethoxylate composition was obtained at a low pressure of 5 mmHg in a boiling point range of 170 to 174° C.

0065

The alkyl chain carbon addition position of the ethoxylate site of the secondary tetradecanol ethoxylate composition thus obtained was calculated using  $^1\text{H-NMR}$  analysis (FIG. 3) and the proton ratio of the alkyl terminal methyl group. The percentage of the secondary alcohol ethoxylate with the ethoxylated second position was 69 mol %. Moreover, the NMR measurement methods and the calculation of the ethoxylation position were carried out just as for Embodiment 1. This secondary alcohol ethoxylate composition had a flow point of -10° C when it was measured according to JIS K-2269.

0066

**Embodiment 4: Secondary Tetradecanol Ethoxylate Ethylene Oxide Addition Composition**

102 g (0.40 mol) of the high-grade, secondary tetradecanol ethoxylate composition produced in Embodiment 3 and 0.2 g of sodium hydroxide (as a catalyst) were placed in a stainless steel autoclave. After the nitrogen replacement, the pressure inside the reactor with the nitrogen was 1.0 kg/cm<sup>2</sup> G. After the contents had been heated to 150° C, 150 g (3.42 mol) of ethylene oxide was run into the autoclave over 3 hours. After that, the contents were held at 150° C for another hour. Following cooling to room temperature, the internal pressure was purged leaving secondary tetradecanol ethoxylate ethylene oxide addition composition where the average value of "n" in the General Formula (1) was 9.6.

0067

The alkyl chain carbon addition position of the ethoxylation site of the secondary tetradecanol ethoxylate ethylene oxide addition composition produced in Embodiment 4 was calculated using the proton ratio of the alkyl terminal methyl group using  $^1\text{H-NMR}$  analysis (FIG. 4) and it was

found that the percentage of the secondary alcohol ethoxylate ethylene oxide addition composition where the second position had been ethoxylated was 66 mol %. The NMR measurement method and the method for calculating the ethoxylation position were the same as for Embodiment 1.

0068

Comparison Example 1: Primary Dodecanol Ethoxylate Ethylene Oxide Addition

320 g (1.7 mol) of n-dodecanol and 0.2 g of sodium hydroxide (as a catalyst) were placed in a stainless steel autoclave and, after the nitrogen replacement, the pressure inside the reactor was brought to 1.0 kg/cm<sup>2</sup> G using nitrogen. The temperature was increased to 150° C and 680 g (15.5 mol) of ethylene oxide was introduced into the autoclave over a period of 3 hours. After the introduction of the ethylene oxide, the autoclave was cooled to room temperature. The internal pressure was then purged, leaving a primary dodecanol ethoxylate ethylene oxide addition where the average value of "n" in the General Formula (1) was 9.0.

0069

Comparison Example 2: Secondary Dodecanol Ethoxylate Composition

810 g (4.82 mol) of 1-dodecene, 900 g (14.52 mol) of monoethylene glycol and 100 g of BEA zeolite (a catalyst manufactured by PQ, Inc, Product Name: VALFOR CP 811 BL-25) were placed in a 3000 ml glass reactor that was equipped with stirring paddles and a circulating cooling system. After the gas was replaced with nitrogen, it was kept at normal pressure in a nitrogen gas atmosphere. Next, the temperature was increased to 150° C while the mixture was being stirred at a speed of 600 rpm. After reacting at that temperature for 3 hours, the reaction solution was cooled to room temperature, the upper layer of dodecene phase was separated off and distilled. The unreacted dodecene was extracted and 255 g of secondary dodecanol ethoxylate was obtained in a vacuum of 2 mmHg and a boiling point of 129 to 131° C.

0070

The alkyl chain carbon addition position of the ethoxylate site of the secondary dodecanol ethoxylate composition was calculated using the proton ratio of the alkyl terminal methyl group and <sup>1</sup>H-NMR analysis (FIG. 5). This showed that the secondary alcohol monoethoxylate percentage where the second position had been ethoxylated was 94 mol %. The method of calculating the ethoxylation position and the NMR measurement methods were the same as in Embodiment 1.

0071

Comparison Example 3: Secondary Dodecanol Ethoxylate Ethylene Oxide Addition

255 g (1.1 mol) of secondary dodecanol monoethoxylate produced in Comparison Example 2 and 0.2 g of sodium hydroxide (as a catalyst) were placed in a stainless steel autoclave. After the nitrogen replacement, the internal pressure of the reactor was brought to 1.0 kg/cm<sup>2</sup> G using nitrogen. After heating to 150° C, 358 g (8.14 mol) of ethylene oxide was introduced into the autoclave over 3 hours. After that, the autoclave was kept at 150° C for another hour. The autoclave was then cooled to room temperature, the internal pressure purged and a secondary dodecanol ethoxylate ethylene oxide addition was produced where the average value of "n" in the General Formula (1) was 8.4.

0072

The alkyl chain carbon addition position of the ethoxylate site of the secondary dodecanol ethoxylate ethylene oxide addition composition produced was calculated using the proton ratio of the alkyl terminal methyl group and <sup>1</sup>H-NMR analysis (FIG. 6). The results showed that the percentage of secondary alcohol ethoxylate where the second position had been ethoxylated was 93 mol %. The method of calculating the ethoxylation position and the NMR measurement methods were the same as in Embodiment 1.

0073

#### Embodiment 5: Secondary Dodecanol Ethoxylate Sulfuric Acid Ester Salt Composition

Using a 100-cm long cylindrical tube with an inside diameter of 5 mm as a tube-shaped reaction cylinder, the secondary dodecanol ethoxylate composition produced in Embodiment 1 was caused to flow downward, forming a thin film, at a speed of 16.2 g per minute along the interior wall of the reaction tube from a container that had been attached to the top of the tube. At the same time, a nozzle attached to the top of the reaction tube was used to introduce anhydrous sulfuric acid that had been diluted with nitrogen gas. The flow speed of the all nitrogen gas into the reaction tube was 30 m per second and the concentration of the anhydrous sulfuric acid in the all mixed gas that was flowing in was 4 wt %. The mol ratio of the secondary dodecanol ethoxylate that flowed down with the anhydrous sulfuric acid was 1.1. The heat that was produced by the reaction of the ethoxylate and the anhydrous sulfuric acid was removed using a cooling medium that flowed around the exterior of the reaction tube. It was kept at 15° C. The liquid that flowed out of the reaction tube was separated into nitrogen gas and the product of the reaction using a cyclone. The product of the reaction was immediately neutralized using a sodium hydroxide aqueous solution, forming an aqueous solution that was approximately 25% sulfuric acid ester salt.

0074

The alkyl chain carbon addition position of the sulfuric acid ester salt of the secondary dodecanol ethoxylate sulfuric acid ester salt composition produced was calculated using the proton ratio of the alkyl terminal methyl group and <sup>1</sup>H-NMR analysis (FIG. 7). The results show that the percentage of secondary dodecanol ethoxylate sulfuric acid ester salt where the second position had undergone sulfuric acid esterization was 66 mol %.

0075

#### Embodiment 6: Secondary Dodecanol Ethoxylate Ethylene Oxide Addition Sulfuric Acid Ester Salt Composition

155 g (0.67 mol) of the secondary dodecanol ethoxylate composition that was an intermediate product in Embodiment 1 and 0.2 g of sodium hydroxide (as a catalyst) were placed in a stainless steel autoclave. After nitrogen replacement, the pressure inside the reactor was brought to 1.0 kg/cm<sup>2</sup> G using nitrogen and heated to 150° C. 62 g (1.41 mol) of ethylene oxide was introduced into the autoclave over a period of 3 hours, after which, the autoclave was kept at 150° C for 1 additional hour. After cooling to room temperature, the internal pressure was purged, leaving a secondary dodecanol ethoxylate ethylene oxide addition composition where the oxyethylene group averaged 3.1 mol.

0076

217 g (0.67 mol) of this secondary dodecanol ethoxylate ethylene oxide addition composition to which ethylene oxide had been added was placed in a 500-ml flask and cooled to 10° C. 86.3 g (0.74 mol) of chlorosulfonate was dripped into this over a period of about 1 hour. During the dripping process, the temperature of the solution was kept between 10 and 15° C. After dripping the chlorosulfonate, a stream of nitrogen gas was placed in the reaction solution and the byproduct hydrogen chloride gas was removed. Next, while maintaining a temperature of 20° C or less, the reaction solution was neutralized by dripping it into a solution of sodium hydroxide, producing an aqueous solution that was approximately 25% sulfuric acid ester salt.

0077

The alkyl chain carbon addition position of the sulfuric ester salt of the secondary dodecanol ethoxylate ethylene oxide addition composition sulfuric acid ester salt composition that was produced was calculated using the proton ratio of the alkyl terminal methyl group and <sup>1</sup>H-NMR analysis (FIG. 8). The results showed that the percentage of secondary dodecanol ethoxylate ethylene oxide addition sulfuric acid ester salt where the second position had undergone sulfuric acid esterization was 75 mol %. The method of calculating the sulfuric acid esterization position and the NMR measurement methods were the same as those for Embodiment 1.

0078

Embodiment 7: Secondary Hexadecanol Ethoxylate Sulfuric Acid Ester Salt Composition

1-hexadecene was processed in 5 wt % BEA zeolite (manufactured by PQ, Inc., Product Name: VALFOR CP 811 BL-25) at 150° C for 13 hours. 810 g (3.62 mol) of the hexadecene isomer mixture (composed of 20 mol % 1-hexadecene and 80 mol % inner hexadecene), 900 g (14.52 mol) of monoethylene glycol and 100 g of catalyst BEA zeolite (manufactured by PQ, Inc, Product Name: VALFOR CP 811 BL-25) were placed in a 3000-ml glass reactor that was equipped with stirring paddles and a circulating cooling system. The gas phase area underwent nitrogen replacement and the nitrogen gas atmosphere was maintained at normal pressure. The temperature was then raised to 150° C while stirring at a speed of 600 rpm. The reaction took place over a 3 hour period at that temperature. The reaction solution was then cooled to room temperature, the upper hexadecene phase layer separated off and distilled. The unreacted hexadecene was extracted leaving 95 g of secondary hexadecanol ethoxylate in a vacuum of 2 mmHg at a boiling point range of 160 to 165° C.

0079

80 g (0.28 mol) of this secondary hexadecanol ethoxylate composition and 400 g of ethylene chloride (as a catalyst) were placed in a 1-liter flask and cooled to 10° C. 36 g (0.31 mol) of chlorosulfonate was then dripped into this over a period of approximately 1 hour. During the dripping process, the temperature of the liquid was kept between 10 and 15° C. After dripping the chlorosulfonate, a stream of nitrogen gas was passed through the reaction solution to remove the byproduct hydrogen chloride gas. Next, the reaction solution was neutralized by dripping it into a sodium hydroxide while keeping the temperature at or below 20° C. The ethylene chloride was then removed, leaving an aqueous solution that was approximately 25% sulfuric ester salt.

0080

The alkyl chain carbon addition position of the sulfuric acid ester salt of the secondary hexadecanol ethoxylate sulfuric acid ester salt composition produced, was calculated using the proton ratio of the alkyl terminal methyl group and  $^1\text{H-NMR}$  analysis (FIG. 9). The results showed that the percentage of secondary hexadecanol ethoxylate sulfuric acid ester salt where the second position had undergone sulfuric acid esterization was 61 mol %. The method of calculating the sulfuric acid esterization position and the NMR measurement methods were the same as those for Embodiment 1.

0081

Comparison Example 4: Primary Alcohol Ethoxylate Ethylene Oxide Addition Sulfuric Acid Ester Salt

593 g (3.08 mol) of primary alcohol (a mixture of n-dodecanol and n-tetradecanol) and 0.2 g of sodium hydroxide (as a catalyst) were placed in a stainless steel autoclave. After nitrogen replacement, the internal pressure in the reactor was brought to 1.0 kg/cm<sup>2</sup> G using nitrogen gas. After raising the temperature to 150° C, 407 g (9.25 mol) of ethylene oxide was introduced into the autoclave over a period of 3 hours. After that, the temperature was maintained at 150° C for 1 additional hour before being cooled to room temperature. After purging the internal pressure, an average of 3.0 mol of ethylene oxide was added, producing a primary alcohol ethoxylate ethylene oxide addition.

0082

200 g (0.62 mol) of this primary alcohol ethoxylate ethylene oxide addition were placed into a 500-ml flask and cooled to 10° C. 79.0 g (0.68 mol) of chlorosulfonate were dripped into this over a period of approximately an hour. During the dripping process, the temperature of the solution was kept between 10 and 15° C. After the chlorosulfonate drip, nitrogen gas was forced through the reaction solution to remove the byproduct hydrogen chloride gas. Next, keeping the temperature at or below 20° C, the reaction solution was dripped into an aqueous solution of sodium hydroxide, neutralizing it. An aqueous solution that was approximately 25% primary alcohol ethoxylate ethylene oxide addition sulfuric acid ester salt was produced.

0083

Embodiment 5: Secondary Dodecanol Ethoxylate Sulfuric Acid Ester Salt-Composition

255 g (1.11 mol) of the secondary dodecanol ethoxylate produced in Comparison Example 2 and 510 g of ethylene chloride were placed in a 1-liter flask and cooled to 10° C. 142 g (1.22 mol) of chlorosulfonate was then dripped into this over a period of approximately 1 hour. During the dripping process, the temperature of the liquid was kept between 10 and 15° C. After dripping the chlorosulfonate, nitrogen gas was passed through the liquid to remove the byproduct hydrogen chloride gas. Next, keeping the temperature at 20° C or lower, the reaction solution was dripped into sodium hydroxide to neutralize it, yielding an aqueous solution that was approximately 25% sulfuric acid ester salt.

0084

The alkyl chain carbon addition position of the sulfuric acid ester salt of the secondary dodecanol ethoxylate sulfuric acid ester salt composition produced was calculated using the proton ratio of the alkyl terminal methyl group and  $^1\text{H-NMR}$  analysis (FIG. 10). The results showed that

the percentage of the secondary dodecanol ethoxylate sulfuric acid ester salt where the second position had undergone sulfuric acid esterization was 94 mol %. The method of calculating the sulfuric acid esterization position and the NMR measurement methods were the same as those for Embodiment 1.

0085

Embodiments 8 and 9, Comparison Examples 6 and 7

We measured the following physical characteristics and surface characteristics on the substances produced in Embodiments 2 and 4 as well as Comparison Examples 1 and 3. Those results are shown in Table 1.

0086

Note that these physical characteristics and surface characteristics were measured using the following measurement methods.

0087

(1) Flow Point

Flow points were measured in accordance with JIS K-2269, the Petroleum Product Flow Point Testing Method.

0088

(2) Permeation

Wool: A 20-ounce piece of roller cross wool measuring 90 x 10 mm (manufacturing by Nippon Keori) was measured at 25° C in accordance with JIS K-3362-1955. (Concentration of Activating Agent: 0.1 wt %)

0089

Cotton: This was measured using the Canvas Disk Method using No. 6 sailcloth at 25° C. (Concentration of Activating Agent: 0.25 wt %)

0090

(3) Foaming State

This was measured in accordance with JIS K-3362, the Ross-Meyers Method at 25 ° C. (Concentration of Activating Agent: 0.1 wt %)

0091

Table 1

Physical Characteristics		Embodiment 2 Sample	Embodiment 4 Sample	Comparison Example 1 Sample	Comparison Example 3 Sample
Flow Point (° C)		8	16	24	9
Permeation (sec)	Wool	5	9	7	6
	Cotton	9	15	14	10
Foaming State (cm)	Right After	163	138	148	158
	5 min later	87	113	135	98

0092

Embodiments 10 through 12, Comparison Examples 8 and 9

We made the following measurements on the substances produced in Embodiments 5 through 7 and Comparison Examples 4 and 5. The results are shown in Table 2.

0093

Note that the physical characteristics were measured using the following methods.

0094

(1) Liquid State Range

The aqueous solution viscosity was measured at 25° C using a Brookfield Rotating Viscometer.

0095

(2) Surface Tension

This was measured at 25° C using the Wilhelmy Method and a surface tension meter manufactured by Kyowa Science. (Concentration of Activating Agent: 0.1 wt %)

0096

(3) Permeation

The same methods were used on cotton as were used for Embodiments 8 and 9. (Concentration of Activating Agent: 0.25 wt %)

0097

(4) Foaming State

The same methods were used as for Embodiments 8 and 9.

0098

Table 2

	Embodiment 5 Sample	Embodiment 6 Sample	Embodiment 7 Sample	Comparison Example 4 Sample	Comparison Example 5 Sample
Liquid State Range (wt %)	45 or less	--	--	30 or less	--
Surface Tension (dyne/cm)	29	36	37	42	33
Permeation (sec) (cotton)	7	12	29	45	8
Foaming State: Right after (cm)	198	183	185	192	187
5 min later	155	21	167	170	157

0099

Embodiments 13 through 17 and Comparison Example 10

We evaluated the detergent capacity of the substances produced in Embodiments 5 through 7 and Comparison Example 3. The results are shown in Table 3.

0100

Note: The following conditions were tested with reference to JIS K-3362, using a stirring detergent tester (Terg-O-tometer).

0101

Washing Conditions

Soiled Cloth Size: 5 x 5 cm

Soiling Substances	Compositional Breakdown (%)
Oleic Acid	28.3
Triolein	15.6
Cholesterol Oleate	12.2
Liquid Paraffin	2.5
Squalene	2.5
Cholesterol	1.6
Gelatin	7.0
Yellow- Red Earth	29.8
Carbon Black	0.5

Water Used: Tap Water

Temperature: 25 °C

Time: Washing: 5 minutes; Rinsing: 5 minutes

Tub Ratio: 3 articles/1 pot (1 liter)

Concentration of Activating Agents: 0.03 %

#### Detergent Capacity Evaluation Methods

Using a reflectometer, the reflectivity (of the original cloth (prior to soiling), the artificially soiled cloth and the cloth after it was washed) was measured in 3 places on each of the pieces of test cloth. The detergent capacity (%) was calculated using the average values and the following formula.

0102

Equation 1

$$\text{Detergent Capacity (5)} = \frac{R_w - R_s}{R_o - R_s} \times 100$$

0103

In the equation,  $R_o$  is the reflectivity of the original cloth,  $R_s$  is the reflectivity of the artificially soiled cloth and  $R_w$  is the reflectivity of the washed cloth.

0104

Table 3

	Embodiment 2 Sample	Embodiment 4 Sample	Embodiment 5 Sample	Embodiment 6 Sample	Embodiment 7 Sample	Comparison Example 3 Sample
Detergent Capacity (%)	80	85	80	78	85	75

0105

Embodiments 18 through 22

We performed the following emulsification capacity evaluations on the substances produced in Embodiments 2 and 4 through 7. The results are shown in Table 4.

0106

Note that the measurements were made using the following methods. 55 ml of water and 40 ml of oil were mixed together and 5 ml of the samples was added. After sufficient mixing, they were left to settle. The separated state of the layer of water or oil was observed after 5 minutes. Evaluations were made as follows using the emulsified state area.

0107

O: Good State of Emulsification

Δ: Some Separation

X: Completely Separated

0108

Table 4

	Embodiment 2 Sample	Embodiment 4 Sample	Embodiment 5 Sample	Embodiment 6 Sample	Embodiment 7 Sample
Emulsification Capacity	O	O	O	O	O
Spindle Oil	O	O	O	O	O
Ethyl Acrylate	O	O	O	O	O
Xylene	O	O	O	O	O

Brief Description of the Drawings

FIG 1.

This is the  $^1\text{H-NMR}$  analysis data used in the calculation of the alkyl chain carbon addition position of the ethoxylation site of the secondary dodecanol ethoxylate composition obtained in Embodiment 1.

FIG. 2

This is the  $^1\text{H-NMR}$  analysis data used in the calculation of the alkyl chain carbon addition site of the ethoxylated area secondary dodecanol ethoxylate ethylene oxide addition composition produced in Embodiment 2.

FIG. 3

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the ethoxylated area of the secondary tetradecanol ethoxylate composition produced in Embodiment 3.

FIG. 4

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the ethoxylated area of the secondary tetradecanol ethoxylate ethylene oxide addition composition produced in Embodiment 4.

FIG. 5

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the ethoxylated area of the secondary dodecanol ethoxylate composition produced in Comparison Example 2.

FIG. 6

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the ethoxylated area of the secondary tetradecanol ethoxylate ethylene oxide addition composition produced in Comparison Example 3.

FIG. 7

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the sulfuric acid ester salt of the secondary dodecanol ethoxylate sulfuric acid ester salt addition composition produced in Embodiment 5.

FIG. 8

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the sulfuric acid ester salt of the secondary dodecanol ethoxylate ethylene oxide addition composition produced in Embodiment 6.

FIG. 9

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the sulfuric acid ester salt of the secondary hexadecanol ethoxylate sulfuric acid ester salt composition produced in Embodiment 7.

FIG. 10

This is the  $^1\text{H-NMR}$  analysis data that was used in the calculation of the alkyl chain carbon addition site of the sulfuric acid ester salt of the secondary dodecanol ethoxylate composition sulfuric acid ester salt composition produced in Comparison Example 5.

FIG. 1

**FIG. 2**

**FIG. 3**

**FIG. 4**

**FIG. 5**

**FIG. 6**

**FIG. 7**

**FIG. 8**

**FIG. 9**

FIG. 10

Continued from the Front Page

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